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A Note on the Formation Mechanism of Shish Kebab Structures (Commemoration Issue Dedicated to Professor Keinosuke Kobayashi on the Occasion of His Retirement)

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CITATION:

Nagasawa, Toshio ...[et al]. A Note on the Formation Mechanism of Shish Kebab Structures (Commemoration Issue Dedicated to Professor Keinosuke Kobayashi on the Occasion of His Retirement). Bulletin of the Institute for Chemical Research, Kyoto University 1977, 55(2): 168-176

ISSUE DATE:

1977-08-31

URL:

<http://hdl.handle.net/2433/76731>

RIGHT:

A Note on the Formation Mechanism of Shish Kebab Structures

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Received March 15, 1977

Three kinds of procedures in crystallization of polyethylene in a solution under a shear stress were carried out in an attempt to get some circumstantial evidence for the judgment of the validity of two controversial models on Shish Kebab structures. In a crystallization process between two glass slides, undeformed rodlike crystals developed from oriented dissolved molecules under no shear stress and typical Shish Kebabs formed from oriented molecules under a shear stress. Summarizing all experimental results, it was made clear that Shish Kebabs were formed by plastic deformation of spirally grown rodlike crystals.

INTRODUCTION

Pennings observed in 1965¹⁾ that fiberlike structures were formed from a stirred polyethylene solution and the term "Shish Kebab" were coined for those structures in view of their morphological features.^{2,3)} In 1970 he proposed a structural model on arrangements of long chain molecules for the Shish Kebab as shown in Fig. 1-A and the formation process of a backbone crystal in the Shish Kebab as shown in Fig. 1-B.⁴⁾ This model consists of a backbone crystal made up of extended polymer chains to which are attached lamellar crystals containing folded polymer chains. On the other hand in 1973 a controversial structural model to Pennings model was proposed by us as shown in Fig. 2,^{5,6)} where long and thin crystals were grown in a stirred solution by screw dislocation growth mechanism like a whisker, then and there those spirally grown crystals were plastically deformed along to the long axis by the stirring force to be Shish Kebab structures.

In recent comments on these two conflicting models for the structure and the formation mechanism, the author noted the validity of those models should be settled by the investigation of the crystal growth mechanism.⁷⁾

This note is purposed to give some circumstantial evidence for the validity of our structural model and to contribute to the understanding of the crystal growth mechanism.

EXPERIMENTAL AND RESULTS

1) Material

Linear polyethylene (Sholex 6009 M) was used in following experiments. The molecular weight was 80,000 as determined by intrinsic viscosity measurements ($[\eta] = 1.35 \times 10^{-3} \text{ M}^{0.63}$)⁸⁾ and the melt index was 0.9.

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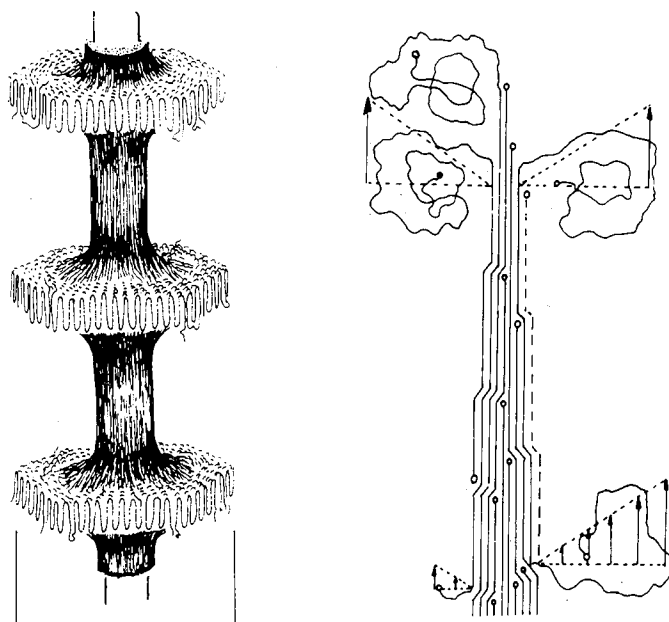


Fig. 1. Pennings' model for a Shish Kebab structure (A) and formation mechanism of a backbone crystal in the Shish Kebab (B).

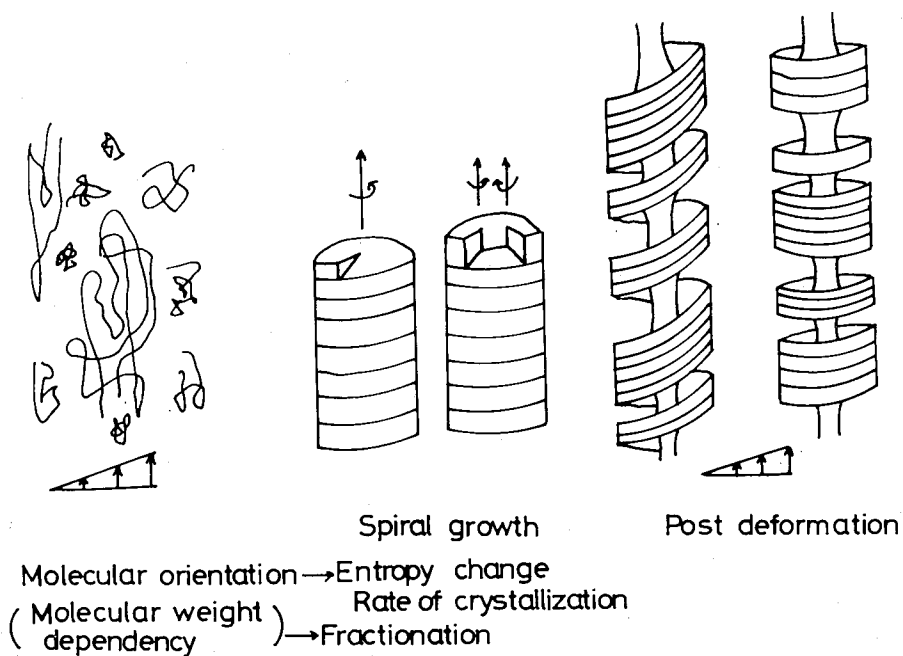


Fig. 2. Spiral growth model for the Shish Kebab structure.

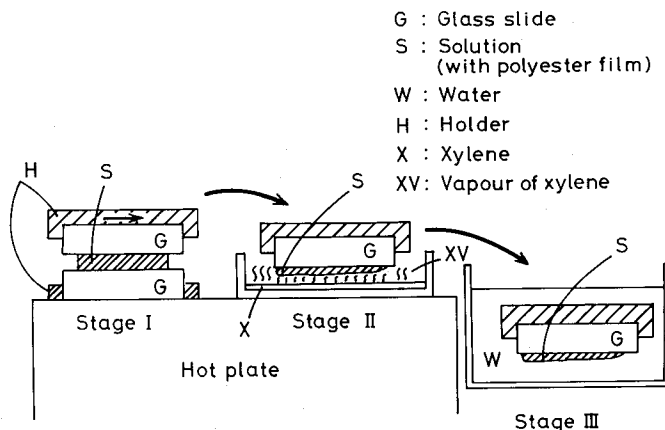


Fig. 3. Procedure of crystallization between two glass slides.

2) Crystallization between Two Glass Slides

A xylene solution of polyethylene (1.0 wt%) at 135°C was sandwiched between two glass slides with twenty microns thick polyester films for the adjustment of the thickness of the solution. When the solution temperature measured by temporarily inserting fine thermocouples reached a fixed temperature (T_c) on a hot plate (Stage I in Fig. 3), a plane shear stress was set up in the polymer solution by translating the upper glass slide at constant speed parallel to the lower glass slide by a synchronous motor drive system (not shown). The separating upper glass slide after being pulled out was held few millimeters above the hot xylene on the hot plate to be exposed to xylene vapour for a fixed time (t) (Stage II in Fig. 3) and then it was suddenly soaked in a water cooling bath (Stage III in Fig. 3). Four experiments were carried out under above mentioned procedure as tabulated in Table I.

The soaked glass slide was dried and prepared for viewing of deposited polymer crystals on the slide surface in the Hitachi transmission electron microscope HU-11.

Table I.

Experiment	T_c (°C)	t (sec.)
A	120	10
B	120	0*
C	95	10
D	95	0*

* very close to zero second

Figure 4 shows fine platelike polyethylene crystals formed in Experiment A and Fig. 5 shows rodlike crystals formed in Experiment B. These two experiments were carried out in an attempt to determine at which stage in Fig. 3 those crystals deposited. On the results, it was reasoned that polyethylene molecules in the solution at 120°C were only oriented without showing a sign of crystallization under plane shear stress at Stage I. In Experiment A the orientation of those dissolved molecules were relaxed during ten seconds period at the Stage II and then those unoriented molecules formed fine platelike crystals at Stage

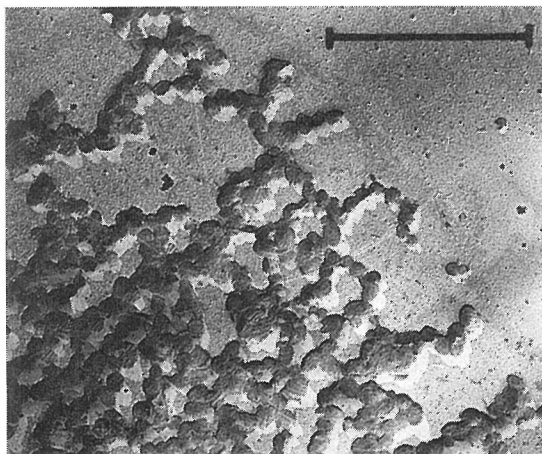


Fig. 4. Platelike polyethylene crystals developed in Experiment A.

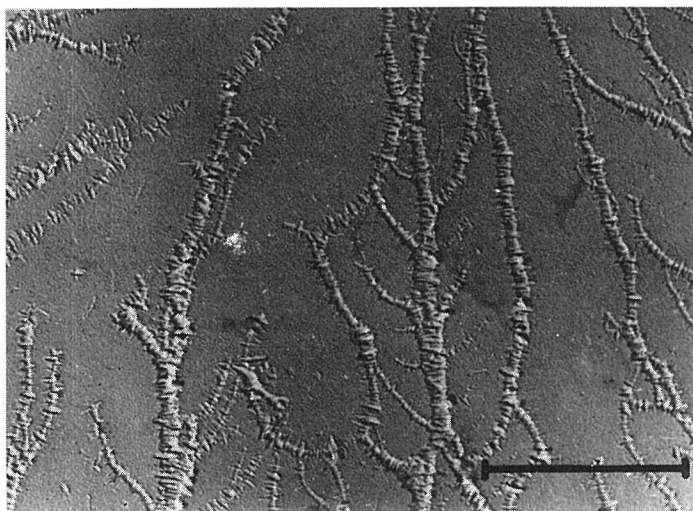


Fig. 5. Rodlike crystals developed in Experiment B.

III. On the other hand in Experiment B those oriented dissolved molecules started to crystallize at Stage III before relaxed and formed rodlike crystals as shown in Fig. 5. Increasing the fixed time t from zero to ten seconds in Experiment B, the morphological feature of crystals were continuously changed from platelike crystals to rodlike crystals. In Experiments C and D, there were no differences in morphological feature of developed crystals and those were typical Shish Kebab structures as represented in Fig. 6. These results are suggesting that polyethylene molecules in a solution at 95°C were oriented under the plane shear stress and also simultaneously started to crystallize at Stage I.

Summarizing all above results, when oriented dissolved molecules in a solution crystallize under no shear stress, they form rodlike crystals as shown in Fig. 5 and when oriented molecules crystallize under a shear stress, developed crystals are deformed by the shear stress and become Shish Kebab structures as shown in Fig. 6.

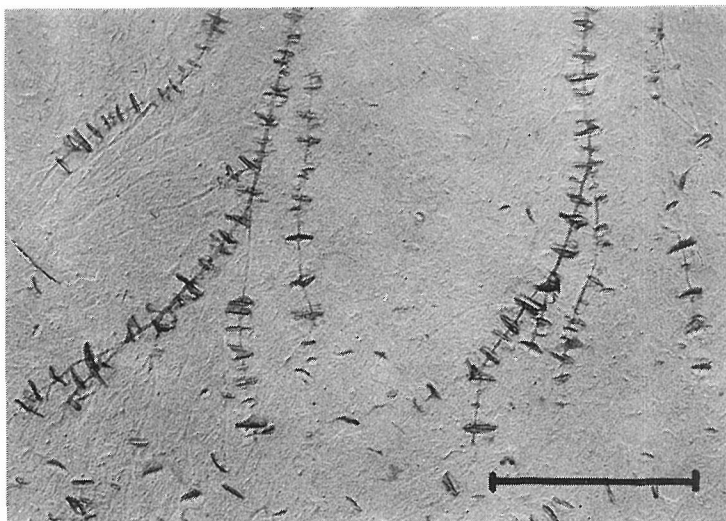


Fig. 6. Shish Kebab structures developed in Experiment C.

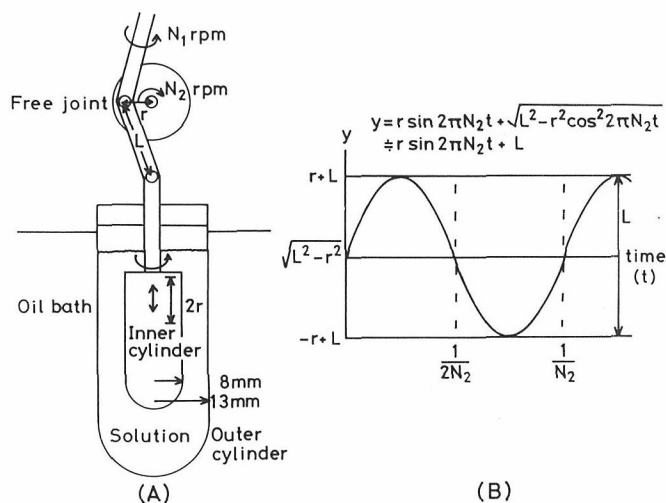


Fig. 7. Schematic diagram of coaxial double cylinders of which the inner cylinder can be simultaneously rotated and oscillated.

3) Crystallization between Coaxial Double Cylinders

A new apparatus with coaxial double cylinders of which the inner one could rotate around a center long axis and concurrently oscillate parallel to the axis as shown in Fig. 7 was developed. A xylene solution of polyethylene (1.0 wt %) at 130°C was filled up into the gap of two cylinders and the temperature was gradually decreased to 97°C at a cooling rate of 0.5°C/min. rotating and oscillating the inner cylinder. Then the inner cylinder was pulled out pouring hot pure xylene on the surface and prepared for viewing in the electron microscope.

Six experiments were carried out as tabulated in Table II.

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Table II.

Experiment	No. of revolutions (N1/min.)	No. of oscillations (N2/min.)
E	750	0
F	300	0
G	100	0
H	50	0
I	750	300*
J	750	750*

* The amplitude (1 in Fig. 7) is 5.0 cm.

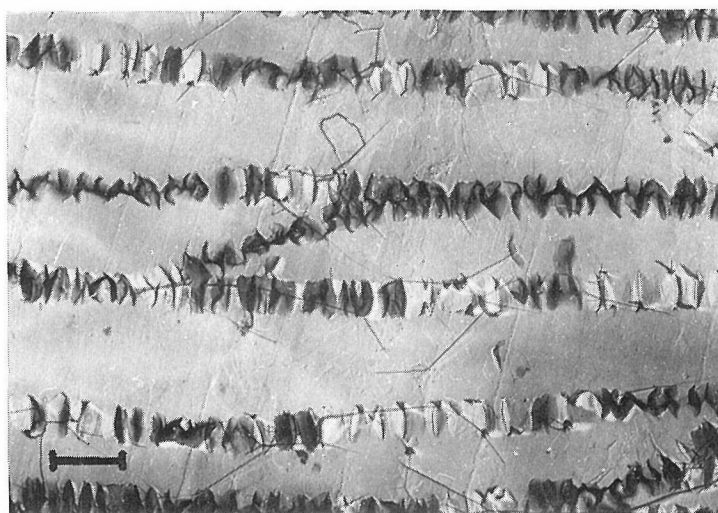


Fig. 8. Produced in Experiment E.

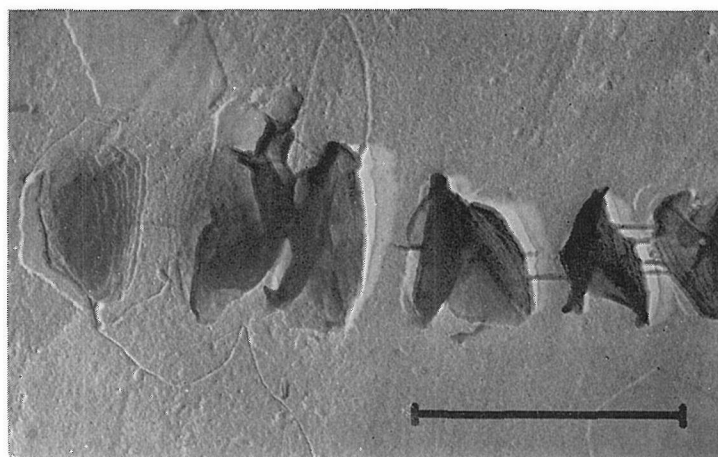


Fig. 9. Produced in Experiment F.

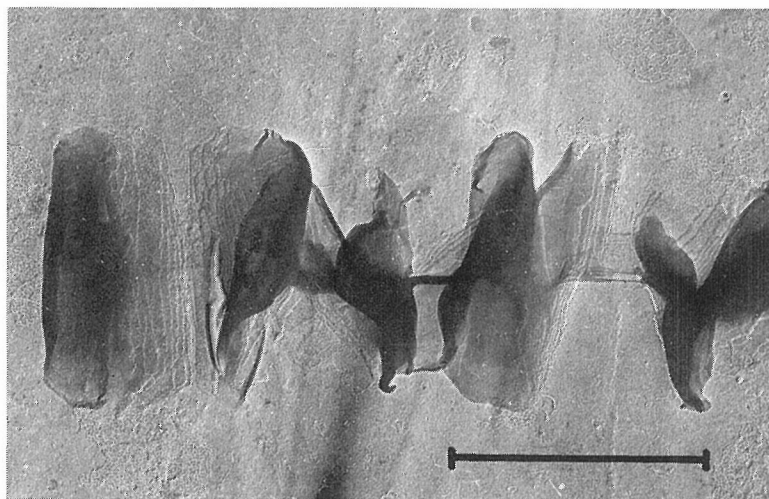


Fig. 10. Produced in Experiment G.

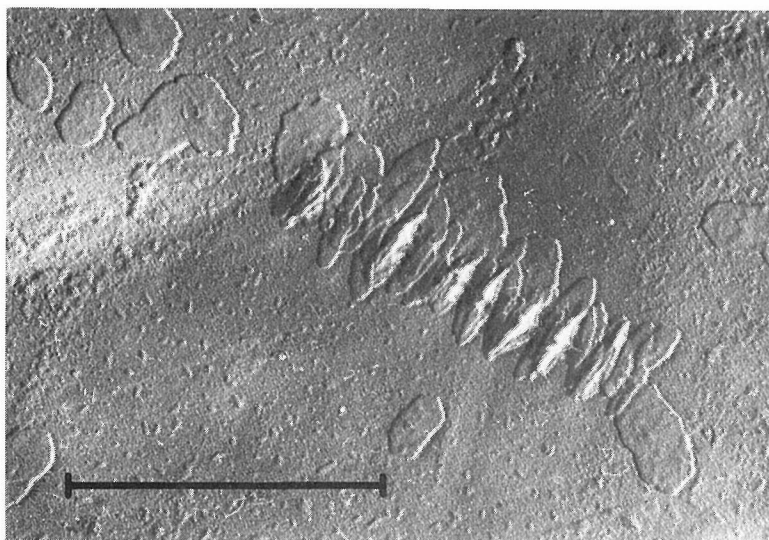


Fig. 11. Produced in Experiment H.

Experiments E, F, and G were carried out in an attempt to observe morphological marks in detail of Shish Kebab structures formed under comparatively low shear stresses. Typical features formed in Experiments E, F, and G are shown in Fig. 8, 9, and 10, where several blocks consisting of piled up lamellar crystals of almost same size are connected with fine fibrils in a row. Each of those blocks seems like a spirally grown crystals as shown in Fig. 9 and 10. These fine fibrils do not straightly pass through several blocks as drawn in Fig. 1-A, but are independently connecting adjacent two blocks. In Experiment H those fine fibrils are no more observed as shown in Fig. 11. It seems that the degree of deformation of deposited crystals is smaller with lower shear stress.

In Experiments I and J many fibrils were formed as shown in Fig. 12 and 13. Those



Fig. 12. Produced in Experiment I. The arrow is indicating the direction of oscillations.

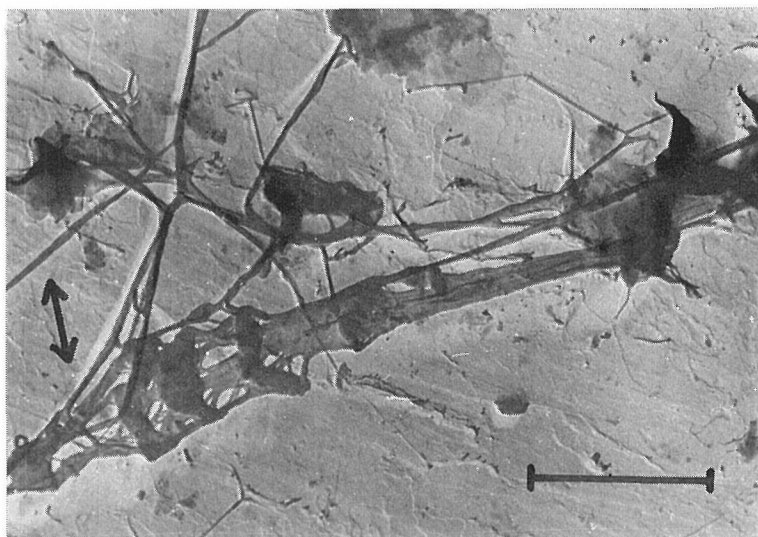


Fig. 13. Produced in Experiment J. The arrow is indicating the direction of oscillations.

fibrils form a line along the direction perpendicular to the long axis of Shish Kebabs, which is parallel to the oscillating direction. This result means that those fibrils were produced as the outcome of plastic deformation by the oscillation of the inner cylinder. In Fig. 13, most of crystals were deformed and only skeltons of Shish Kebabs were remained.

All these results are suggesting that Kebabs of Shish Kebab structures are undeformed part of piled up lamellar crystals grown by spiral growth mechanism and Shish were formed by plastic deformation of a part of Kebab as Fig. 2 illustrates the mechanism.

CONCLUSION

All above experimental results are supporting our model drawn in Fig. 2 for the formation mechanism of Shish Kebabs. Original forms of Shish Kebabs, rodlike structures in Fig. 5, are very similar to the structure formed from a oriented polymer melt.⁹⁾ This fact is suggesting that a basic principle controls the crystallization process of oriented polymer molecules in both solution and melt.

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